

STO - Gaussian Overlap Notes

10/07/2025

Oceanside, CA



Index

1. Slater Type Orbitals	3
2. Gaussian Type Orbitals	3
3. Overlap Integrals	4
3.1 s-s	5
3.2 s-p	5
3.3 p-s	6
3.4 p-p	6
4. Quadrature	6

1. Slater Type Orbitals

Slater Type Orbitals (STO) in the atomic orbital (AO) basis are used in semiempirical methods based on Neglect of Differential Diatomic Overlap (NDDO) such as AM1. STO are given by:

$$X_{nlm}(\vec{r}_A) = N_n(\xi) r_A^{n-1} e^{-\xi r_A} Y_{lm}(\theta_A, \phi_A), \quad (1)$$

with normalization:

$$N_n(\xi) = \left(\frac{(2\xi)^{2n+1}}{(2n)!} \right)^{1/2}, \quad (2)$$

where ξ is the orbital exponent (parameter depending on the given orbital and semiempirical method such as AM1), n is the principal quantum number, \vec{r}_A is the correspondent distance to the nucleus, and $Y_{lm}(\theta_A, \phi_A)$ are the normalized real harmonics. In these notes we'll only consider s and p types of orbitals:

$$(l=0, m=0) \rightarrow |1s\rangle = \frac{(2\xi)^{1/2}}{((2n)!)^{1/2}} r^{n-1} e^{-\xi r} \frac{1}{\sqrt{4\pi}}, \quad (3)$$

$$(l=0, m=1) \rightarrow |1p_x\rangle = \frac{(2\xi)^{1/2}}{((2n)!)^{1/2}} r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \quad (4)$$

$$\frac{(2\xi)^{1/2}}{((2n)!)^{1/2}} r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}} \frac{y}{r}, \quad (5)$$

$$\frac{(2\xi)^{1/2}}{((2n)!)^{1/2}} r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}} \frac{z}{r}, \quad (6)$$

where x , y , and z are the Cartesian coordinates in the coordinate system centered in the corresponding atom.

2. Slater Type Orbitals

A primitive Cartesian Gaussian Orbital is typically written as:

$$\phi_{l_x l_y l_z}^{(A)}(\vec{r}, \alpha) = N(l_x, l_y, l_z, \alpha) x^{l_x} y^{l_y} z^{l_z} e^{-\alpha r^2}, \quad (7)$$

where the total angular degree is $\ell = \ell_x + \ell_y + \ell_z$, α is the Gaussian exponent, and the normalization factor is given by:

$$N(\ell_x, \ell_y, \ell_z, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \sqrt{\frac{(8\alpha)^{\ell_x + \ell_y + \ell_z} \ell_x! \ell_y! \ell_z!}{(z\ell_x)! (z\ell_y)! (z\ell_z)!}}, \quad (8)$$

For s type GTO we get:

$$\phi_s(\vec{r}, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}, \quad (9)$$

while for p type GTO we get:

$$\phi_{p_x}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}} x e^{-\alpha r^2}, \quad (10)$$

$$\phi_{p_y}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}} y e^{-\alpha r^2}, \quad (11)$$

$$\phi_{p_z}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}} z e^{-\alpha r^2}, \quad (12)$$

3. Overlap Integrals

For deriving tractable equations for the overlap integrals we'll use the following identity (Gauss Transform):

$$e^{-Rr} = \frac{1}{\sqrt{\pi}} \int_0^\infty u^{-3/2} e^{-\xi^2/4u} e^{-ur^2} du, \quad (13)$$

representing the Slater exponential as a continuous superposition of Gaussians.^[5] We'll also use the Gaussian product theorem:

$$e^{-ur_A^2} e^{-ur_B^2} = \exp(-\mu r^2) \exp[-(1+\alpha)(r-P)^2], \quad (14)$$

where:

$$P = \frac{uA + \alpha B}{u + \alpha}, \quad (15)$$

and:

$$\mu = \frac{u\alpha}{u+\alpha}, \quad (16)$$

3.1 S-S

Evaluating eq.(8) and eq.(9) in displaced atomic centers \vec{A} and \vec{B} such that $\vec{R} = \vec{A} - \vec{B}$, and $R = |\vec{R}|$, using the Gauss Transform eq.(13), swapping the integration operators, solving for the spatial integral, and using the identity:

$$\int_0^{n-1} e^{-kra} = (-\frac{\partial}{\partial k})^{n-1} e^{-kra}, \quad (17)$$

we get:

$$S_{SS}^{(m)}(R, \xi, \alpha) = N_{n0}(k) N_s(\alpha) \pi z^n \int_0^{\infty} \frac{u^{-(n+1)}}{(u+\alpha)^{3/2}} e^{-\frac{2k}{u+\alpha} R^2} e^{-\frac{\xi^2}{4u}} H_n\left(\frac{\xi}{z\sqrt{u}}\right) du, \quad (18)$$

where:

$$N_{n0}(k) = \left(\frac{(2\xi)^{2n+1}}{(2n)!} \right)^{1/2}, \quad (19)$$

and:

$$N_s(\alpha) = \left(\frac{2\alpha}{\pi} \right)^{3/4}, \quad (20)$$

and H_n is the Hermite polynomial!

3.2 S-P

Analogously, by using eqs. (10-12), we get:

$$S_{SP_R}^{(m)} = N_{n0}(k) N_p(\alpha) \pi z^n R \int_0^{\infty} \frac{u^{-(n+1)}}{(u+\alpha)^{5/2}} e^{-\frac{2k}{u+\alpha} R^2} e^{-\frac{\xi^2}{4u}} H_n\left(\frac{\xi}{z\sqrt{u}}\right) du, \quad (21)$$

where:

$$N_p(\alpha) = \frac{(2\xi)^{5/4}}{\pi^{3/4}} \sqrt{2}, \quad (22)$$

3.3 p-s

Analogously we get:

$$S_{p-s}^{(n)} = -N_{S(p)}(\xi) N_{S(p)}(\alpha) \pi 2^{-(n-1)} R_k \int_0^\infty \frac{u^{-n/2}}{(u+\alpha)^{3/2}} e^{-\frac{\pi \alpha}{u+\alpha} \xi^2} e^{-\frac{\xi^2}{4u}} H_{n-1}\left(\frac{\xi}{2\sqrt{u}}\right), \quad (23)$$

where:

$$N_{S(p)}(\xi) = \left(\frac{(2\xi)^{2n+1}}{(2n)!} \right)^{1/2} \sqrt{\frac{3}{4\pi}}, \quad (24)$$

3.4 p-p

Using eqs.(4-6) and eqs.(10-12) we get:

$$S_{p-p}^{(n)}(\xi) = N_{S(p)}(\xi) N_p(\alpha) \pi 2^{-(n-1)} \int_0^\infty \frac{u^{-n/2}}{(u+\alpha)^{3/2}} e^{-\frac{\pi \alpha}{u+\alpha} \xi^2} e^{-\frac{\xi^2}{4u}} H_{n-1}\left(\frac{\xi}{2\sqrt{u}}\right) \times \\ \times \left[\left(-\frac{\alpha}{u+\alpha} R_k \right) \left(\frac{u}{u+\alpha} R_k \right) + \frac{\delta_{k\ell}}{z(u+\alpha)} \right] du, \quad (25)$$

4. Quadrature

In order to calculate numerically the relevant integrals, let's introduce the following substitution:

$$u = \frac{\xi^2}{4t}, \quad (26)$$

$$du = -\frac{\xi^2}{4t^2} dt, \quad (27)$$

for which the integrals become:

$$\int_0^\infty e^{-\frac{t}{4}} G(t) dt, \quad (28)$$

where:

$$G(t) = t^{-(\alpha+2)} \left(1 + \frac{4t\zeta}{\xi^2}\right)^{-b} \exp\left[-\frac{\alpha R^2 \xi^2 t}{4t\zeta + \xi^2}\right] H_m(\sqrt{t}) A\left(\frac{\xi^2}{4t}, R\right), \quad (29)$$

where:

$$ss \quad s - p_k \quad p_k - s \quad p_k - p_{k'}$$

$$N \quad N_{no}(s) N_s(s) \pi i^{-n} \quad N_{no}(s) N_p(s) \pi i^{-n} R_k \quad -N_{stop}(s) N_s(s) \pi i^{-n-1} R_k \quad N_{stop}(s) N_p(s) \pi i^{-n-1}$$

$$a \quad -\frac{(n+1)}{2} \quad -\frac{(n-1)}{2} \quad -\frac{n}{2} \quad -\frac{n}{2}$$

$$b \quad \frac{3}{2} \quad \frac{5}{2} \quad \frac{5}{2} \quad \frac{3}{2}$$

$$m \quad n \quad n \quad n-1 \quad n-1$$

$$A(h, R)$$

$$-\frac{4\alpha \xi^2 t}{(4t\zeta + \xi^2)} R_k R_{k'} + \frac{2t}{4t\zeta + \xi^2} \delta_{kk'}$$

Finally, the integral in eq.(28) can be calculated by means of the Gauss-Laguerre node/weights:

$$\int_0^\infty e^{-t} G(t) dt = \sum_{i=1}^N w_i G(t_i), \quad (30)$$

Tip: Use N=32 as a default and check against 48 and 64 for convergence when developing

References

- [1] James J. P. Stewart, "Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and applications to 70 elements", *J. Mol. Model.* (2007) 13: 1173-1213.
- [2] Miguel A. Blanco, M. Flórez, M. Bermejo, "Evolution of rotation matrices in the basis of real spherical harmonics", *Journal of Molecular Structure (Theochem)* 419 (1997) 19-29.
- [3] André Severo Pereira Gómez, Rogelio Custodio, "Exact Gaussian Expansions of Slater Type Atomic Orbitals", *Journal of Computational Chemistry*, 23, 10 (2007) 1007-1012.